

10/517799

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



13 DEC 2004



(43) International Publication Date
8 January 2004 (08.01.2004)

PCT

(10) International Publication Number
WO 2004/002672 A1

(51) International Patent Classification⁷: **B23K 26/38**

(21) International Application Number:
PCT/US2003/014468

(22) International Filing Date: 6 May 2003 (06.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0214990.4 28 June 2002 (28.06.2002) GB

(71) Applicant (for all designated States except US): **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **LOW, David, K., Y.** [SG/SG]; Block 277, Bangkit Road, #08-114, 670277 Singapore (SG).

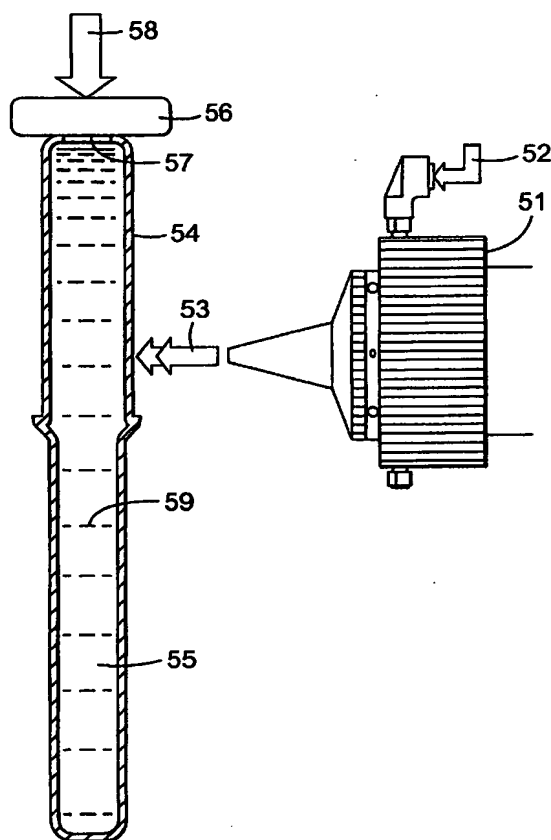
(74) Agents: **RINGSRED, Ted, K.** et al.; Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,

[Continued on next page]

(54) Title: MANUFACTURE OF VALVE STEMS



(57) Abstract: A method for providing a hole into a valve component having an internal cavity (55), said method comprising the steps of filling and sealing a fluid (59) within said cavity; and laser drilling the hole through the component into the internal cavity. Said method is particularly advantageous for providing a side port into a valve stem (54). The present invention also relates to a method of manufacturing a valve stem, said method comprising the steps of: a) providing a valve stem work-piece having a passageway with an outlet (57); b) filling the passageway with a fluid; c) sealing the outlet; d) laser drilling a side port through the work-piece into the passageway; and e) unsealing the outlet.

WO 2004/002672 A1

WO 2004/002672 A1



SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— with international search report

Manufacture of Valve Stems

Technical Field

The present invention relates generally to improvements in the manufacture of valve components, in particular valve stems for pharmaceutical aerosol valves, in particular for metered dose dispensing valves. The present invention also relates to the provision of valve stems having desirable structural qualities and/or blockage resistance.

Background of the Invention

The use of aerosols to administer medicament has been known for several decades. Such aerosol formulations generally comprise medicament, one or more propellants, (e.g. chlorofluorocarbons and more recently hydrogen-containing fluorocarbons, such as propellant 134a ($\text{CF}_3\text{CH}_2\text{F}$) and propellant 227 ($\text{CF}_3\text{CHF}\text{CF}_3$)) and surfactant and/or a solvent, such as ethanol.

Pharmaceutical aerosols for inhalation, nasal, sublingual administration, generally comprise a container or vial of the aerosol formulation equipped with a metered dose dispensing valve. Although there are many different designs of metered dose valves, the majority comprises a metering chamber and a valve stem that slides through a diaphragm, also known as an outer stem gasket or seal, into the metering chamber. When the valve is in its non-dispensing position, the diaphragm maintains a closed seal around the valve stem. The valve stem includes a side port in communication within a passageway inside the valve stem. When the valve is actuated, the side port slides past the diaphragm and into the metering chamber, and the contents of the metering chamber pass through the side port and passageway, exiting the stem outlet.

The diameter of the side port can range from 0.1 to 0.8 mm, while the stem outlet diameter typically ranges from 0.8 to 3 mm. The central passageway typically has a diameter from 0.8 to 4 mm.

It will be appreciated that the aerosol valve as well as the aerosol formulation, each play an important part in obtaining optimum pharmaceutical properties from the product. For example, there should be no blockage of the valve, in particular the valve stem, which could impair or prevent medicament delivery.

5

Valve stems have conventionally been constructed by injection molding thermoplastics and by deep drawing metal. Metal valve stems may also be fabricated by machining and/or cold forging.

10 Deep drawn metal valve stems are hollow having a central bore from the closed end of the valve stem to the outlet end of stem, which acts the passageway. Typically the outlet end is curved inwardly restricting the size of the central bore at the outlet. The side port is generally formed by punching. This operation results in a circumferential projection or burr being formed around the side port within the valve stem. In some cases, the metal
15 punched out to form the side port may not be completely removed leaving a large burr projecting inwardly into the valve stem. It has been observed, in particular for ethanol-containing medicinal aerosol formulations, that there is a tendency for drug to build up in areas where it cannot be readily dislodged, e.g. such projections or burrs around the side port. A large medicament build-up and/or any subsequent dislodgement thereof could
20 cause complete blockage of the valve stem. Furthermore, the tendency for ethanol to evaporate is far higher at the openings to the atmosphere, e.g. the valve stem side port. Thus, there is a tendency for medicament build-up in these regions, which could lead to blockage of the side port.

25 It has been reported that although it is possible to insert a die prior to punching the side port in order to minimize the formation of the burr within the valve stem. This technique leaves a sharp edge around the side port on the inner as well as the outer surface of the valve stem. The sharp edge on the outer surface is prone to damaging the diaphragm seal associated with the valve stem.

30

WO 99/55600 discloses metered dose valves having a machined and/or cold forged, preferably stainless steel, valve stem in which blockage problems are substantially reduced. The valve stems are preferably fabricated by machining and/or cold forging and then drilling with a drill bit the passageway including the outlet as well as the side port. To avoid the formation of burrs around the side port within the valve stem, it is described to preferably insert and remove the drill bit at least twice during the drilling operation.

Laser drilling of valves stems to provide the side port has been reported in The Aerosol Handbook (M. Johnsen, 2nd Edition, 1982, Wayne Dorland Co. p 164.) However, it is reported that by using laser beams, side ports as small as 0.13 mm have been made, but they are highly subject to clogging and other problems.

Summary of the Invention

There is an ongoing need for a method for providing a side port in a valve stem, in particular allowing for the provision of a valve stem having desirable structural qualities and/or blockage resistance.

Surprisingly, we have found that by filling and sealing a fluid, such as water, into the passageway of the valve stem and then laser drilling a side port into the valve stem, a side port, and hence a valve stem having desirable structural qualities and/or blockage resistance can be provided.

It has been found that a number of defects occur during conventional laser drilling of valve stems. Backwall damage occurs due to impingement of excess laser beam on the backwall, when the laser beam breaks through the wall being drilled. Due to the accumulation of re-solidified material on the periphery of the orifice exit, dross forms around the side port within the valve stem. Furthermore, downwardly ejected melt can also lead to the deposition of particles on the interior surface of the valve stem, in particular on the backwall. In valve stems, these defects can provide undesirable surfaces for medicament build-up or attachment of loose medicament particles, and thus increasing the tendency of

blockage in the valve stem. These defects may also enhance the possibility and/or onset of corrosion within metal valve stems.

It has been found that by filling a fluid into the valve stem passageway and sealing the stem outlet, to substantially prevent the fluid from escaping through the outlet (before and during laser drilling of the side port, backwall damage as well as the formation of dross and deposited particles can be significantly reduced or substantially prevented. The reduction or substantial prevention of the damage seems to be the result from two aspects. First, by temporarily sealing the stem outlet, upon beam breakthrough, the fluid is initially held within the passageway (e.g. it is not simply pushed or blasted through the outlet) as a barrier, absorbing and diffusing excess laser beam and thus substantially preventing impingement of the laser on the backwall, as well as impeding the deposition of particles. Secondly, after beam breakthrough, at least a part of the fluid (vaporized and/or as fluid) and, if any assist gas used in the laser drilling process, assist gas are then forced to escape or are pushed out the newly laser-drilled hole, hindering the formation of dross accumulation at the hole exit and again deposition of particles.

The interior of valve stems thus laser drilled, exhibit desirable structural and/or blockage resistance qualities. In particular, the side port exit within the valve stem, which is free or substantially free of dross and does not exhibit a circumferential projection or a sharp edge, exhibits an advantageous minimum of potential seeding surface for medicament deposition or build-up and thus exhibits advantageous blockage resistance properties.

Accordingly, in one aspect of present invention there is provided a method for providing a hole into a valve component having an internal cavity, said method comprising the steps of filling and sealing a fluid within said cavity; and laser drilling the hole through the component into the internal cavity.

This method of laser drilling is desirably suitable for drilling a hole in any valve component having an internal cavity. However the method is particularly advantageous for providing a side port in a valve stem and in the manufacture of valve stems.

Another aspect of the present invention is the provision of a method of manufacturing a valve stem, said method comprising the steps:

- a) providing a valve stem work-piece having a passageway with an outlet;
- 5 b) filling the passageway with a fluid;
- c) sealing the outlet;
- d) laser drilling a side port through the work-piece into the passageway; and
- e) unsealing the outlet.

10 Desirably laser drilling is performed in conjunction with an assist gas.

Methods according to the present invention are applicable for plastic or metal valve components or valve stems, respectively.

15 Valve components/stems thus laser-drilled may be suitably subjected to cleaning and/or finishing procedures conventionally used for such cleaning and/or finishing.

Alternatively or in addition thereto, valve components/stems thus laser-drilled may be subjected to an abrasive or chemical cleaning or finishing process to remove any spatter
20 which may have formed on the outer surface of the respective component during laser-drilling, e.g. about the periphery of the hole entry, as a result of outwardly ejected melt. For metal valve components/valves, it has been found that when oxygen is preferentially used as an assist gas, any spatter and/or stray re-solidified particles are typically present in the form of a metal oxide and such oxide can be conveniently dissolved in an acid
25 washing. Advantageously the use of such an acid washing as chemical cleaning process can also simultaneously bring about a desirable passivation of the metal surface.

Another aspect of the present invention is a valve stem obtainable according to a method described above.

30

An additional aspect of the present invention is a valve stem obtained according to a method described above.

5 In a further aspect, the invention provides a metered dose valve comprising such a valve stem. In yet another aspect, the invention provides a metered dose dispenser comprising such a valve stem.

The dependent claims define further embodiments of the invention.

10 The invention, its embodiments and further advantages will be described in the following with reference to the following drawings.

Brief Description of the Drawings

Figure 1 shows a cross-section through a metered dose aerosol dispenser.

15 Figure 2 shows a cross-section through a deep drawn metal valve stem of the prior art.

Figure 3 shows a cross-section through a machined and/or cold forged metal valve stem of the prior art.

20 Figure 4 shows scanning electron microscopy (SEM) micrographs of the underside (hole exit) of side ports in (a) a deep drawn valve stem made of Stainless Steel type 305 ("SS 305") and (b) a machined SS 305 valve stem, both after barrel-cleaning.

25 Figure 5 represents schematically and pictorially (a) a preferred method for laser drilling a side port in a valve stem work-piece and (b) a resulting valve stem thereof.

30 Figures 6 (a) and (b) show SEM micrographs of a SS 305 valve stem obtained in accordance with a preferred method of the invention (in particular in accordance to Example 1).

Figure 7 (a) and (b) show SEM micrographs of a SS 305 valve stem obtained after conventional laser-drilling (Example A).

Figure 8 shows a cross-section through a deep drawn metal valve stem obtained through a preferred method of manufacturing a valve stem.

Figure 9 illustrates schematically a preferred system for laser drilling a side port in a valve stem.

Figures 10 (a) and (b) show SEM micrographs of a SS 305 valve stem obtained after laser-drilling a work-piece filled with water but without sealing the outlet (Example B).

Detailed Description of Invention

It is to be understood that the present invention covers all combinations of particular and preferred aspects of the invention described herein.

Figure 1 shows a typical metered dose aerosol dispenser (1), in particular a metered dose inhaler. As illustrated in the dispenser of Figure 1, such a dispenser generally includes a canister (2) equipped with a metering dose valve (generally indicated by (5)), defining a formulation chamber (3), which contains an aerosol formulation (4). The valve (5) typically comprises a ferrule (6) having a central portion retaining the components of the valve and a circumferential flange for crimping around the neck of an aerosol container to secure the valve to the container. A gasket (8) is clamped between the neck of the aerosol container and ferrule ensuring a gas-tight seal. The valve comprises a valve stem (generally shown at (10)) extending through a central aperture (9) in the ferrule through a metering chamber (12). The outer end (14) of the valve stem projects from the metering chamber (12) and is in sealing engagement with elastomeric diaphragm (16). The inner end (20) of the valve stem projects through the metering chamber (12) in sealing engagement with a tank seal (22). A spring (24) is positioned within the metering chamber, one end abutting the tank seal (22) and the other end abutting a flange (26) extending around an intermediate portion of the valve stem. The spring (24) urges the valve stem to

its non-dispensing position as shown in Figure 1. The dispenser may include a retaining cup (28), which extends around the metering chamber (12). (Often, it is desirable to use a retaining cup, when the aerosol formulation is a suspension, while for solution aerosol formulations typically a retaining cup is not applied.) The walls of the retaining cup define a retention chamber (27) and an aperture (29) allowing open communication between the retention chamber and the formulation chamber.

In its non-dispensing position, contents of the retention chamber or, if a retaining cup is not used, the formulation chamber, may enter the metering chamber (12) by passing through the groove (32) on the inner end (20) of the valve stem through the inlet aperture (30) of the metering chamber. When the valve stem is moved to its dispensing position (not shown) the groove (32) passes outside the tank seal (22) and thus the inner end of the valve stem completes a seal preventing flow of aerosol formulation into and out of the metering chamber through the filling end. In its dispensing position, the side port (34) of the valve stem passes through the diaphragm into the metering chamber. The side port (34) is in communication with a central outlet passageway (see Figures 2 and 3) allowing the contents of the metering chamber to be dispensed from the valve.

Figure 2 represents a cross-section through a conventional deep drawn valve stem, which has been used in a metered dose dispensing valve. The valve stem (10) comprises a closed end (43), an outer portion (14), an inner portion (20), a flange (26), groove (32) and side port (34) as described with reference to Figure 1. The valve stem is hollow having a central passageway (40). The outlet end (42) of the valve stem is curved inwardly restricting the size of the central passageway (40) at the outlet (41). The side port (34) is typically formed by punching. Figure 4 (a) shows a SEM micrograph of a typical underside (hole exit) of such a punched side port after barrel cleaning. As can be seen from Figure 4(a), the punching operation results in a circumferential projection with a number of burrs being formed around the side port projecting inwardly into the valve stem. As described above, the projection and burrs can act as a seeding surface for deposition and/or accumulation of medicament, and thus increasing the tendency of the valve stem to block.

Figure 3 represents a cross-section through a machined and/or cold-forged valve stem. Machined valve stems of the type shown in Figure 3 have been used in metered dose dispensing valves. The valve stem (10) comprises an outer end (14), inner end (20), flange (26), groove (32), side port (34) and central passageway (40). The side port and central passageway are formed by drilling with a drill bit and are arranged such that the side port joins the passageway near the inner end of the passageway. To avoid the formation of burrs, the drill bit is typically inserted and removed at least twice during the drilling operation. Figure 4 (b) shows a SEM micrograph of a typical underside (hole exit) of side port in such a machined valve stem after barrel cleaning. As can be seen from Figure 4(b), the underside of the side port exhibits a substantially better structural quality than that of the punched side port of deep drawn valve stems. Although blockage problems are substantially reduced with such machined valve, as can be seen in Figure 4 (b) such bit-drilling leaves a sharp edge around the side port on the interior surface of the valve stem. This edge may also provide a seeding surface for medicament deposition.

Referring to Figure 5(a), which illustrates pictorially a preferred method for laser drilling a hole in a work-piece (54), here in particular a deep drawn metal stem work-piece, the cavity or passageway (55) of the work-piece is filled with a fluid (59), the outlet (57) of the work-piece is sealed, and the hole or side port is laser-drilled (direction of laser beam is generally indicated by the arrows (53)) through the work-piece into the cavity or passageway. Preferably the laser drilling is performed in conjunction with an assist gas (arrow (52) generally indicates the assist gas input near the laser output aperture (51)). Preferably, the outlet (57) of the work-piece is sealed with a mechanical constriction (56), which is held in place by an applied force (as generally indicated by the arrows (58)). Suitably after laser drilling, the outlet is unsealed (not illustrated). The resulting valve stem (10) with the side port (34) is shown Figure 5(b).

Figure 6(b) shows a SEM micrograph of a typical underside (hole exit) of side port provided in accordance with methods of the present invention. It is to be noted that Figure 6 shows micrographs of a valve stem (of Example 1 described below) taken off press without any subsequent cleaning or finishing. As can be readily seen in Figure 6(b), in

particular in comparison to Figures 4(a) and (b), the underside of the side port shows very desirable structural properties, being free of burrs, a circumferential projection and a sharp edge typical of known valve stems used in metering valves.

5 Also in comparison to a side port obtained by conventional laser drilling, the undersides of side ports as well as valve stems obtained accordance methods of present invention show very desirable structural qualities. Figure 7 shows SEM micrographs of a valve stem, in particular the backwall of the valve stem (Figure 7(a)) and the hole exit of the side port (Figure 7(b)) obtained by conventional laser drilling (i.e. Example A described below). As
10 can be seen in a comparison of Figures 6(b) and 7(b) of the side port undersides, the hole exit of the conventional laser drilled side port is irregular with accumulated dross and extensive particle deposition is observed on the underwall about the hole exit, while the hole exit of side port obtained in accordance with the invention is substantially free of dross and the underwall is substantially free of deposited particles. As can be seen in a
15 comparison of Figures 6(a) and 7(a) of the backwall of the valve stems, the backwall of the conventional laser drilled valve stem shows extensive damage and deposited particles, while the backwall of valve stem drilled in accordance with the invention is substantially free of backwall damage and deposited particles.

20 Due to the desirable structural properties of the interior of valve stems laser drilled in accordance with methods of the invention, the valve stems are substantially free of seeding surfaces for the deposition or accumulation of medicament and hence show enhanced blockage resistance. Methods in accordance with the invention of filling and sealing within a cavity a fluid prior to laser drilling can be also advantageously used in providing a hole
25 in other valve components having a cavity (besides valve stems). For example the method can be desirably used to provide aperture(s) in a retaining cup or a metering chamber.

Diameters for the laser-drilled hole or side port may suitably range from 0.1 to 1.1 mm: for side ports of valve stems, more particularly 0.3 to 0.8 mm and most particularly 0.35 to
30 0.75 mm, and for apertures in retaining cups and metering chambers, more particularly 0.6 to 1.0 mm and most particularly 0.75 to 0.95 mm.

Desirably laser drilling is performed in conjunction with an assist gas. Suitable assist gases include assist gases conventionally used in laser drilling, such as oxygen, argon, nitrogen, helium or air. For laser-drilling metal valve components/stems, oxygen as assist gas is preferred.

For ease in manufacturing and processing, the fluid is desirably a fluid at ambient temperature (e.g. about 22°C). Preferably the fluid is a liquid or a liquid-based fluid (e.g. solutions, suspensions, gels, colloidal dispersions including foams, emulsions and sols); more preferably a liquid or liquid-based fluid having a dynamic viscosity less than 33000 mPa's, preferably determined according to Standard Test Method ASTM D2196-99 (Test method A). Water and aqueous fluids are particularly suitable.

In methods of manufacturing plastic valve stems, the valve stem work-piece may be suitably provided by molding, in particular injection thermoplastic molding. More particularly, a valve stem blank having one or more exterior contours of the valve stem may be provided by molding, in particular by injection thermoplastic molding, while the passageway and outlet may be formed by drilling, in particular by laser drilling.

In methods of manufacturing metal, preferably stainless steel, valve stems, the valve stem work-piece may be suitably provided by machining and/or cold forging. More particularly, a valve stem blank having one or more exterior contours of the valve stem can be provided by machining and/or cold forging, while the passageway and outlet may be formed by drilling, in particular by laser drilling.

Alternatively, in the manufacturing of metal, preferably stainless steel, valve stems, the valve stem work-piece may be desirably provided by deep drawing. Preferably the work-piece is deep drawn having one or more exterior contours of the valve stem. For deep drawn valve stems, blockage resistance can be advantageously further enhanced by reducing dead volume within the valve stem, so that aerosol formulation only contacts and passes through the portion of the valve stem necessary to convey the formulation to the

outlet (i.e. between the side port and the outlet of the valve stem). Desirably the manufacture of deep drawn valve stems include steps of: inserting into the passageway a plug, such that a portion of the interior of the passageway between the closed end of the valve stem and the side port is sealed off; and curling the outlet end of the stem inwardly.

5 More desirably the plug is inserted, such that the interior of the valve stem from the closed end of the valve stem and substantially up to the side port is sealed off. The plug may be inserted either before or after laser drilling the side port, more particularly either before the passageway is filled or after the outlet is unsealed. The curling of the outlet end may also be performed either before or after laser drilling, more particular either before sealing the
10 outlet or after unsealing the outlet, but in every case after the plug has been inserted.

Figure 8 shows a cross-section of a preferred deep drawn valve stem obtainable by such a method. As can be seen in the preferred embodiment of Figure 8, the plug (46), which forms an interference fit within the valve stem, is located between the closed end (43) and the side port (34) (more substantially just below the side port). This advantageously
15 reduces the amount of dead volume within the valve stem, thus enhancing blockage resistance. Preferably the plug is made of stainless steel.

Valve components/stems thus laser-drilled may be suitably subjected to cleaning and/or finishing procedures conventionally used for the cleaning and/or finishing, such as bright
20 annealing, barreling or passivation for metal stems. Barreling is typically performed by tumbling a plurality of valve stems in a container with a water and detergent mixture; the detergent is typically a mixture of anionic and non-anionic surfactants and organic acids. In passivation, a metal (in particular stainless steel) valve stem is washed with acid to enhance the formation of a protective, passive metal (chromium) oxide film. Accordingly
25 the valve stems are preferably treated with an acid solution of nitric acid (at 5 to 50% concentration) or citric acid (1 to 10% concentration) or other appropriate compound to remove surface contamination so as to enhance spontaneous passivation.

Alternatively or in addition thereto, valve components/stems thus laser-drilled may be
30 subjected to an abrasive or chemical cleaning or finishing to remove any spatter or stray residual particles. Suitable abrasive cleaning or finishing may include buffing, shot-

blasting or washing with acids. The latter two exemplary cleaning methods are particularly suitable for metal valve component/stems, and the use of acid washing as a cleaning method is particular advantageous when the laser drilling was performed in conjunction with oxygen assist gas. In shot blasting the outer surface is blasted, preferably spot blasted, with fine particles, such as alumina having a particle size of 10 to 100 μm , under high pressure, such as 3 to 5 bar for about 1 to 2 seconds. Desirably a metal pin or shaft may be inserted into the component/stem behind the laser-drilled hole to protect the backwall of the component/stem during the shot blasting.

Due to their desirable structural qualities, valve components/stems obtainable and provided according to the methods of the invention are particularly suitable for use in metering valves, especially metering valves for the delivery of medicament, as well as metered dose dispensers, in particular medicinal metered dose dispensers, more particularly metered dose inhalers.

Examples

Materials used

Valve Stem Work-piece All the following laser drilling experiments were performed with Stainless Steel valve stem work-pieces manufactured by deep drawing out of Stainless Steel Type 305 ("SS 305") strip. The stems had an overall length of 24.4 mm, wall thickness 0.2mm, an external flange between the open portion and the closed portion as well as an external groove. The central bore or passageway had an internal diameter of 2.4 mm at the position where the side port was to be drilled. Unless stated otherwise, the outlet end of the stem was curled inwardly and the outlet had a diameter of 1.6 mm. The internal volume of the stem was 85 microlitres. During the deep drawing process, the steel was coated with drawing oil (ADFORMAL™ EP 130 see below), which was not removed prior to laser drilling.

Tap Water

Gel: Aqua-Gel™ II Cable Pulling Lubricant, supplied by Ideal Industries Inc.

Deb™ hand-washing fluid, supplied by Deb Limited.

Oil: Adformal™ EP130 extreme pressure metal forming oil, supplied by BP Lubricants and Special Products Limited.

Stainless steel shaft with a diameter of 2.2 mm

Plastic-coated wire with a diameter of 1.5 mm

5 Polytetrafluoroethylene (PTFE) sheet with a width of 2.2 mm

Blu-Tack™ – a low tack adhesive putty manufactured by Bostik Limited, Leicester, UK.

10

Laser Drilling

An ElectroX Scorpion 400 W pulsed Nd:YAG laser (supplied by ElectroX, Letchworth, UK), emitting at 1.06 µm wavelength, was used to drill holes in the valve stem work-pieces.

15

20

25

Figure 9 illustrates schematically the arrangement of the laser drilling system (100) used for the following examples. The laser beam (127) was generated by the source (120), which was operated by a hand-held controller (121). The beam was conveyed by an 8 m long, 600 µm core diameter optical fibre (122) that was end-connected to the fibre output tube (123). The fibre output housing (124) contained the fibre output tube, lenses, e.g. the focussing lens (126), and an assist gas nozzle that was supplied by an assist gas input (125). Any excess drawing oil that had been on the work-piece was blown away by the assist gas leaving a thin film on the outer surface. The work-piece (54) was clamped in a vice on a platform (129). The fibre output housing (124) was mounted on a 3-axis CNC table (130) by a mounting (128), which was movable relative to the platform (129) with a traverse range of 500 x 540 x 165 mm³ and a maximum traverse speed of up to 300 mm/s. Such movement was controlled from a personal computer (131) via a CNC table controller (132).

30

A focusing lens with a focal length of 120 mm was used in all the experiments. The focal plane position was placed on the material surface with a nozzle-work-piece distance of 1.7

mm. The target hole size was 0.47 mm diameter. Experiments were carried out with the laser positioned vertically or horizontally, with the stem work-piece correspondingly positioned horizontally or vertically, respectively. It is to be appreciated that the positioning of the laser and work-piece does not have a material effect on the results of the laser drilling. However for the examples in which the stem work-piece was filled with a fluid it is convenient to have the stem work-piece positioned vertically with then the laser positioned horizontally.

In the examples in which the stem work-piece was filled with a fluid, the fluid was injected into the valve stem blank using a 10 ml syringe with a 1.27 mm diameter regular-bevel point needle. In the examples in which the stem opening was sealed, a compressible stem-constriction was pressed onto the stem-opening before and during laser drilling. The stem-constriction was created by placing a piece of Blu-TackTM at the stem-opening and pressing physically with the index finger. In an automated process, the stem-constriction could be made from silicone rubber, such as used to make O-rings:

It was found in preliminary experiments that, to drill a hole in AISI 305 Stainless Steel stem work-pieces having a wall thickness 0.2 mm, a single or a double laser pulse was effective. However, a double pulse of 7 kW peak power was preferred because it produces more consistent holes. In the experiments that follow, a double pulse of 7 kW peak power, a pulse width of 0.3 ms, energy per pulse 2.1 J and pulse frequency of 20 Hz were used, unless otherwise stated. An assist gas, oxygen unless stated otherwise, at a pressure of 3 bar (42 liters per minute flow rate) unless indicated otherwise, was also used. A rectangular pulse shape was used.

Analysis

In order to analyze the laser-drilled valve stems a precision cutter was employed to section along the valve stems. After the stems were sectioned for a length of 17 mm, the stems were physically split open to reveal the underwall (underside) and backwall of the stems. On the underwall of the stems the extent of dross deposition around the hole exit was analyzed; while the backwall was analyzed for any damage as a result of the impingement

of excess laser beam. Both samples were analysed for scattered particle deposition. Preliminary analysis was carried out with an optical microscope. Further analysis was then carried out using a scanning electron microscope (SEM).

Examples 1 to 10 and Examples A to ETable 1

Example	Barrier	Constriction	Laser Position	Assist gas	Pulse width (ms)	Frequency (Hz)
A	None	None	Vertical	O ₂	0.3	20
B	Water	None	Horizontal	O ₂	0.4	20
1	Water	Yes	Horizontal	O ₂	0.4	20
2	Water	Yes	Horizontal	O ₂	0.3	20
C	Pumped Water	None	Horizontal	O ₂	0.4	20
D	Water jet spray	None	Vertical	O ₂	0.3	20
3	Water	Yes	horizontal	O ₂ (1 bar)	0.4	20
4	Water	Yes	horizontal	O ₂ (2 bar)	0.4	20
5	Water	Yes	horizontal	O ₂ (4 bar)	0.4	20
6	Water	Yes	horizontal	O ₂ (6 bar)	0.4	20
7	Water	Yes	horizontal	O ₂	0.4	100
8	Water	Yes	Horizontal	N ₂	0.5 (peak power of 5.4 kW)	20
E	Water	None	Horizontal	N ₂	0.5 (peak power of 5.4 kW)	20
9	Water	Yes	horizontal	Ar	0.4	20
10	Water	Yes	horizontal	Ar	0.5	20

5

Example A:

Figures 7 (a) and (b) show SEM micrographs of a SS 305 valve stem laser-drilled without the use of any barrier material. As can be seen from Figure 7 (a), the backwall was damaged by the excess laser beam leaving behind a damaged spot of about 1 mm and a significant amount of particle deposition. From Figure 7 (b), it can be noted that a significant amount of dross was accumulated on the hole exit.

10

Example B

In this example, tap water was filled into work-piece before laser-drilling. However no stem constriction was used. Figures 10 (a) and (b) show SEM micrographs of a resulting SS 305 valve stem after laser drilling the side port. As can be seen from Figure 10 (a), local backwall damage of approximately 1mm diameter could be noted. The dross accumulation around the hole exit is extensive, with large particles clinging to periphery of the hole exit as can be seen in Figure 10(b).

Examples 1 and 2

Figures 6 (a) and (b) show SEM micrographs of SS 305 valve stems obtained by laser-drilling work-pieces, whose outlet were sealed with a stem constriction after filling the work-piece with water (Example 1). Comparing the results with those of drilling without any barrier or with water but without sealing (Examples A and B), it can be seen that damage to the backwall as well as deposition of particles on the backwall were prevented. No discernible accumulation of dross around the periphery of the hole exit could be noted (as shown in Figure 6 (b)). In addition, the underwall of the stem appears to be substantially free from particle deposition. The results of Example 2, in which a pulse width of 0.3 ms, instead of 0.4 ms was used, were similar to Example 1. In Examples 1 and 2 and all other following examples in which a fluid was filled and sealed within the cavity of the stem work-piece, it was noted that after beam breakthrough, fluid within the stem was pushed out of the newly drilled hole in form of a fan-like spray.

The results of these experiments as well as the results of examples C to E and examples 3-10 are summarized in the following table.

Table 2

Example.	Results		
	Dross	Backwall Damage	Particle Deposition
A	Yes	≈ 1 mm spot	Significant
B	Yes	≈ 1 mm spot (melt)	Significant
1	No, minimal	None	No, minimal
2	No, minimal	None	No, minimal
C	Yes	≈ 2 mm spot (melt)	Some
D	Yes	≈ 1 mm spot	Some
3	No, minimal	None	No, minimal
4	No, minimal	None	No, minimal
5	No, minimal	None	No, minimal
6	No, minimal	None	No, minimal
7	No, minimal	None	No, minimal
8	No, minimal	None	No, minimal
E	Yes	≈ 1 mm spot	Some
9	No, minimal	None	No, minimal
10	No, minimal	None	No, minimal

Example C:

Using a 10 ml syringe fixed to a 1.27 mm diameter regular-bevel point needle, water was 'pumped' into the stems before and during laser drilling in order to continuously fill water into stems even when and after beam breakthrough occurs. The results, were similar to those of Examples A and B, an about 2 mm diameter spot backwall damage was noted together with a significantly amount of dross at the hole exit. Some particle deposition was noted.

Example D:

Throughout the laser drilling a water jet spray was directed into the opening of the valve stem, using an airbrush, at approximately 20 psi. The nozzle of the airbrush was held at distance of 10 mm to the opening of the stem. The results, were similar to those of Examples A to C, an about 1 mm diameter spot backwall damage was noted together with a significantly amount of dross at the hole exit and some particle deposition.

Thus, local backwall damage and particle deposition were prevented completely using the stem constriction, thus providing a cleaner drilling than drilling with no such constriction. In addition, the underwall of the stem appeared to be substantially free from particle deposition and no discernible accumulation of dross around the periphery of the hole exit could be noted when using the stem constriction.

Examples 3-6 - Use of different assist gas pressures of oxygen, i.e. lower pressures of 1 and 2 bars as well as higher pressures of 4 and 6 bar all gave optimal results, showing no significant difference to the results of Examples 1 and 2 performed with an assist gas pressure of 3 bar.

Example 7 - The use of a higher pulse frequency did not affect the results. Again the resulting valve stem was free or substantially free of backwall damage, particle deposition and dross accumulation.

Examples 8 to 10 and E - The results for Examples 8 to 10 were similar to those of Examples 1 to 7, while the results of example E were similar to example B. Thus, the use of nitrogen or argon assist gas in conjunction with constricting the stem outlet also allows the production of valve stems whose interior showed desirable structural qualities, free or substantially free of backwall damage, particle deposition and dross accumulation at the hole exit.

Examples 11 to 13 and Examples F and G

Other fluids, such as gels, oils, solutions were examined as summarized in Table 3.

Table 3

Example	Barrier	Constriction	Laser Position	Assist gas	Pulse width (ms)	Frequency (Hz)
11	Gel	Yes	horizontal	O ₂	0.3	20
F	Gel	None	horizontal	O ₂	0.3	20
12	Oil	Yes	horizontal	O ₂	0.3	20
G	Oil	None	horizontal	O ₂	0.3	20
13	Deb™ fluid	Yes	horizontal	O ₂	0.3	20

5

The results are these experiments are listed below:

Table 4

Example	Results		
	Dross	Backwall Damage	Particle Deposition
11	No, minimal	None	No, minimal
F	Yes	Some, spot mainly melt	No, minimal
12	No, minimal	Very faint, not clearly visible on SEM	No, minimal
G	Yes	≈ 0.4 mm spot mainly melt.	Minimal
13	No, minimal	None	No. minimal

10

The use of other fluids together with sealing the outlet with a stem constriction was equally effective, backwall damage, particle deposition, dross accumulation were either completely prevented or reduced considerably in comparison to results of the examples in which no stem constriction was applied.

Comparative H to J

15

Solids as barriers were examined as summarized in the following table. In each case the barrier was inserted into the cavity of the work-piece before drilling. For examples I and J,

the outlet end of the stem work-piece was not curled, and thus the outlet had a diameter of about 2.4 mm in order to allow the insertion of the PTFE sheet and Stainless Steel ("SS") shaft.

5 **Table 5**

Example	Barrier	Constriction	Laser Position	Assist gas	Pulse width (ms)	Frequency (Hz)
H	Plastic wire	None	Vertical	O ₂	0.3	20
I	PTFE sheet	None	Vertical	O ₂	0.3	20
J	SS shaft	None	horizontal	O ₂	0.4	20

The results are summarized in Table 6.

Table 6

Example	Results		
	Dross	Backwall Damage	Particle Deposition
H	Yes	≈ 0.5 mm spot (melt)	Significant
I	Yes	None	Significant
J	Yes	None	Significant

10 Although in certain cases, the use of a solid barrier prevented backwall damage, in each case significant amounts of dross accumulation and particle deposition (in particular on the underwall) were noted for the resulting valve stems.

Claims

- 5 1. A method for providing a hole into a valve component having an internal cavity,
said method comprising the steps of filling and sealing a fluid within said cavity; and
laser drilling the hole through the component into the internal cavity.
- 10 2. A method for providing a hole according to claim 1, wherein the valve component is a
valve stem.
- 15 3. A method of manufacturing a valve stem, said method comprising the steps of :
a) providing a valve stem work-piece having a passageway with an outlet;
b) filling the passageway with a fluid;
c) sealing the outlet;
15 d) laser drilling a side port through the work-piece into the passageway;
e) unsealing the outlet.
- 20 4. A method of manufacturing a valve stem according to claim 3, wherein the valve stem
is plastic and the valve stem work-piece is provided by molding, in particular by
injection thermoplastic molding.
- 25 5. A method of manufacturing a valve stem according to claim 3, wherein the valve stem
is plastic and the step of providing a valve stem work-piece includes the steps:
i) providing a valve stem blank having one or more exterior contours of the valve stem
by molding, in particular by injection thermoplastic molding; and
ii) forming the passageway and outlet by drilling.
- 30 6. A method of manufacturing a valve stem according to claim 3, wherein the valve stem
is metal and the valve stem work-piece is provided by machining and/or cold forging.

7. A method of manufacturing a valve stem according to claim 3, wherein the valve stem is metal and the step of providing the valve stem work-piece includes the steps:

i) providing a valve stem blank having one or more exterior contours of the valve stem by machining and/or cold forging;

5 ii) forming the passageway and outlet by drilling.

8. A method of manufacturing a valve stem according to claim 5 or claim 7, wherein the passageway and outlet are formed by laser drilling.

10 9. A method of manufacturing a valve stem according to claim 3, wherein the valve stem is metal and the valve stem work-piece is provided by deep drawing.

10. A method of manufacturing a valve stem according to claim 9, wherein the method further comprises the steps

15 f) inserting into the passageway a plug, such that a portion of the interior of the passageway between the closed end of the valve stem and the side port is sealed off; and

g) curling outlet end of the stem inwardly,

wherein the step (f) of inserting the plug is performed either before step b) or after step

20 e) and wherein the step (g) of curling the outlet end is performed either before step b) or after step e), but after inserting the plug.

11. A valve stem obtainable according to the method of any one of claims 2 to 10.

25 12. A valve stem obtained according to the method of any one of claims 2 to 10

13. A metered dose valve comprising a valve stem according to claim 11 or claim 12.

14. A metered dose dispenser comprising a valve stem according to claim 11 or claim 12.

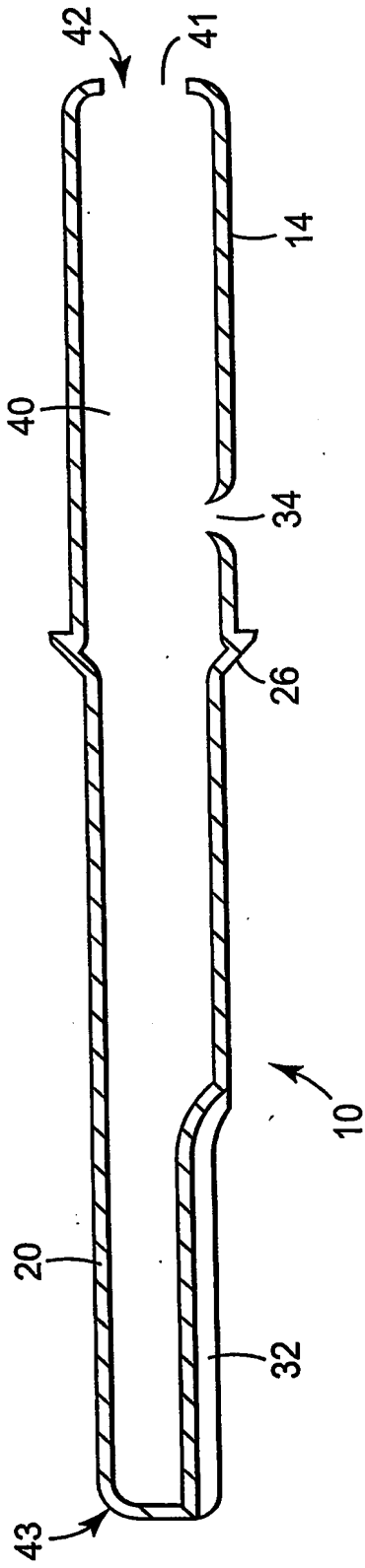


FIG. 2

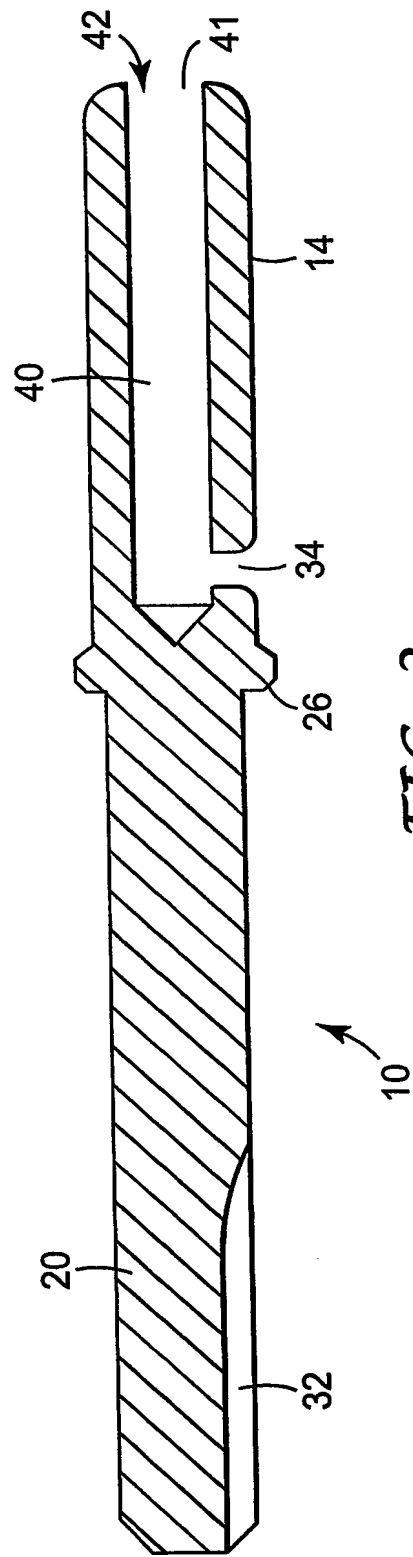


FIG. 3

3/9

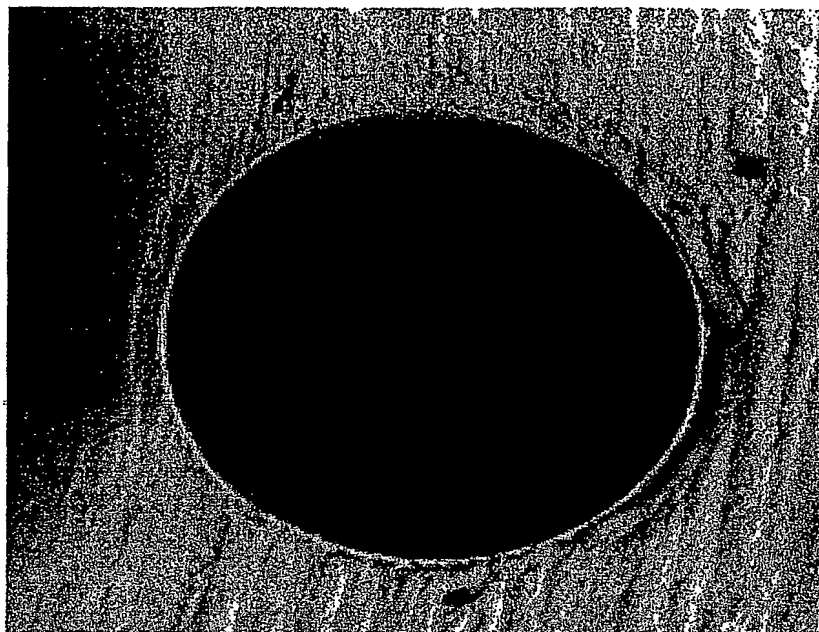


FIG. 4b

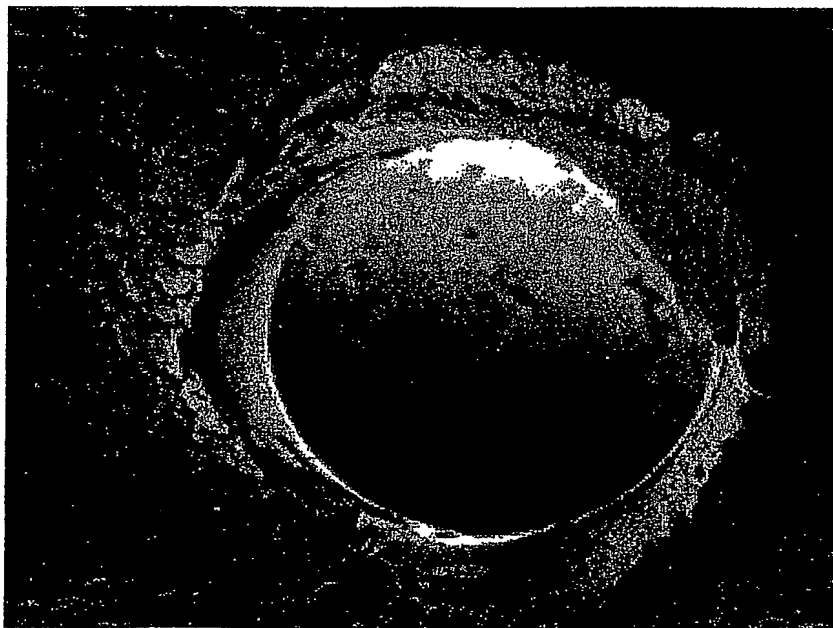


FIG. 4a

BEST AVAILABLE COPY

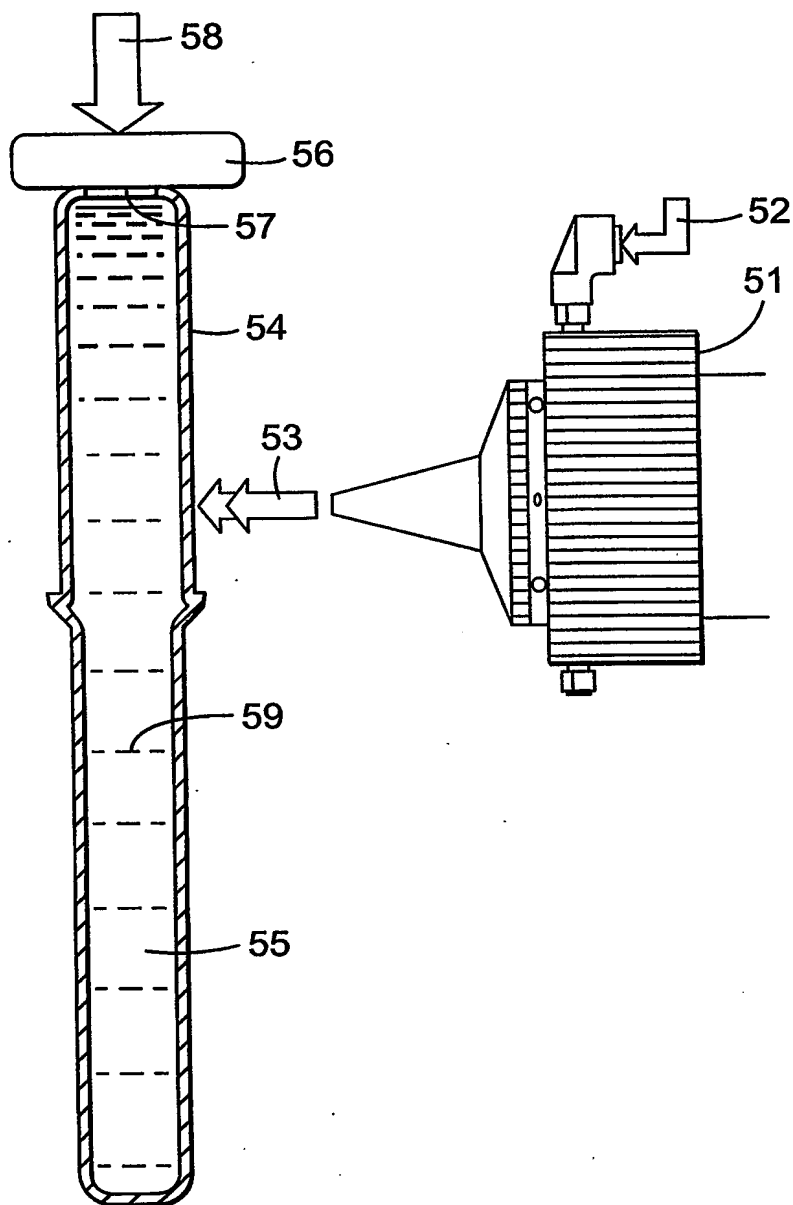


FIG. 5a

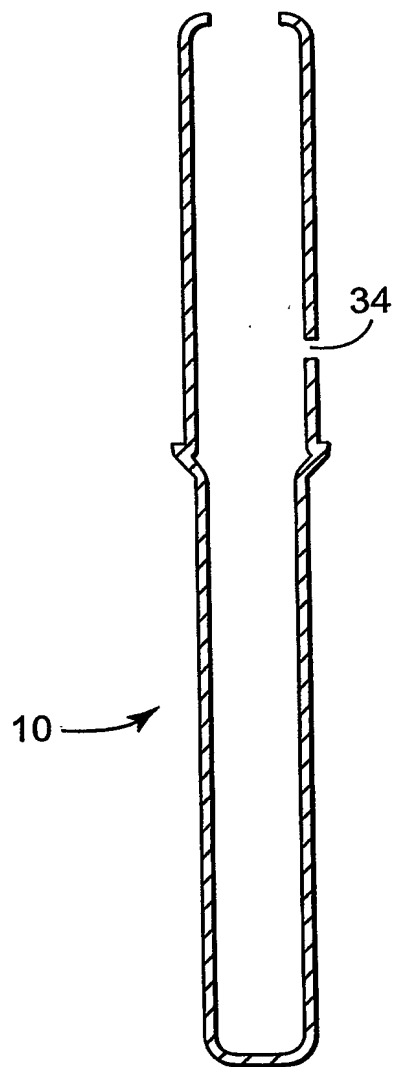


FIG. 5b

5/9

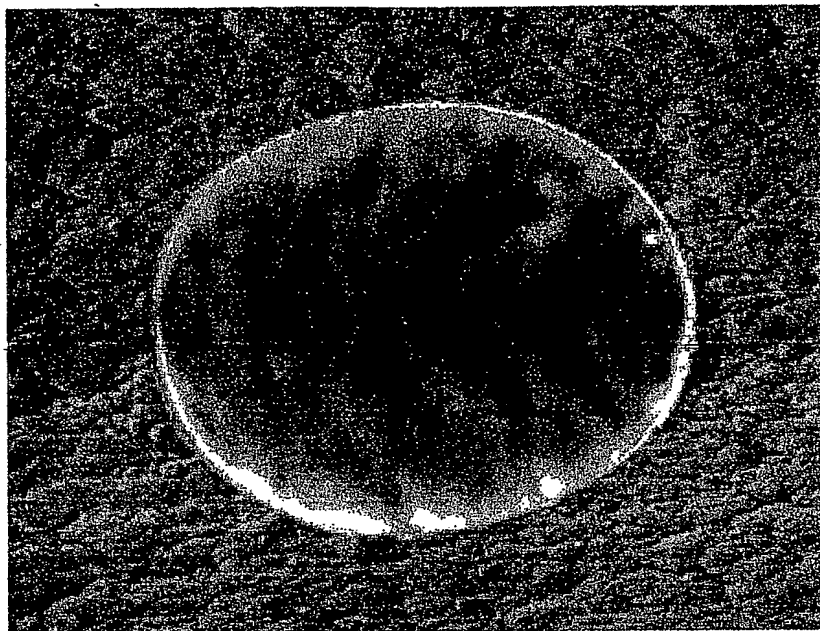


FIG. 6b

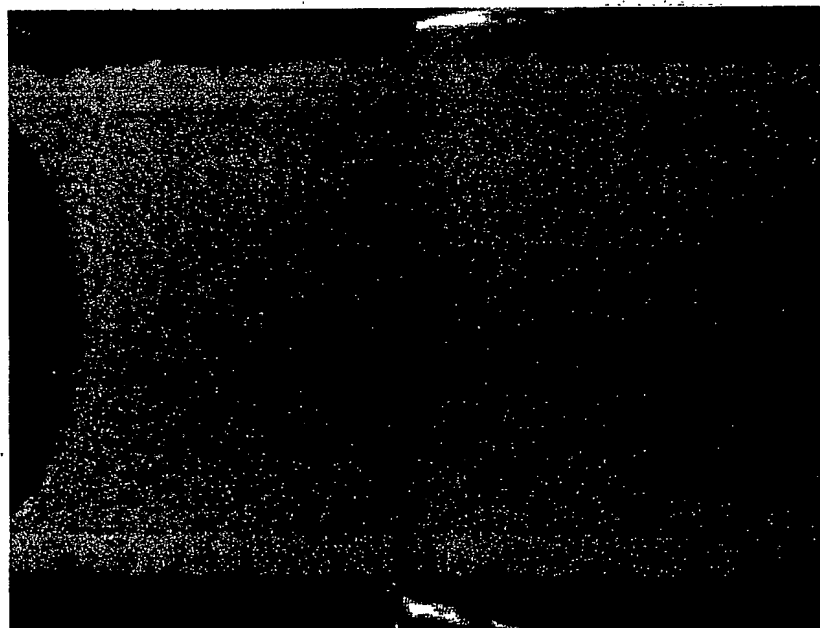


FIG. 6a

BEST AVAILABLE COPY

FIG. 7a

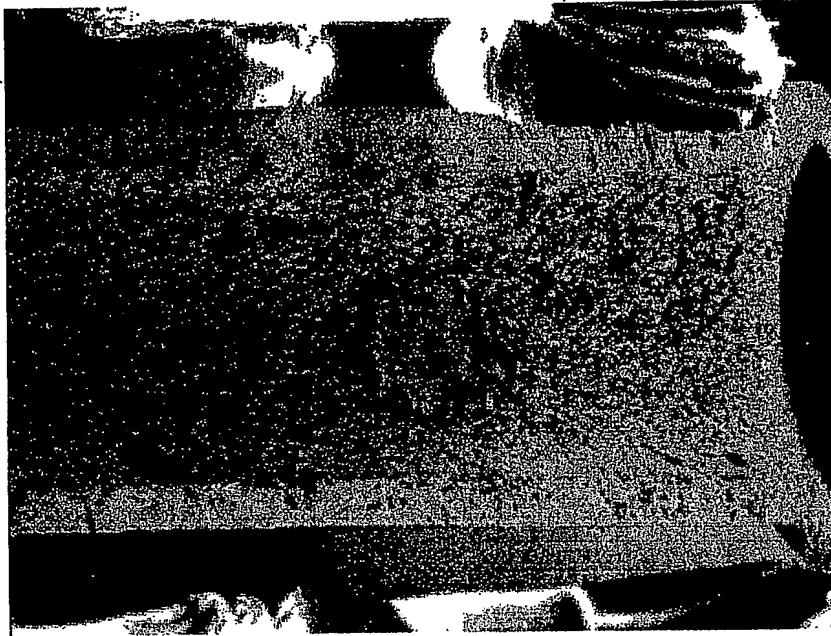
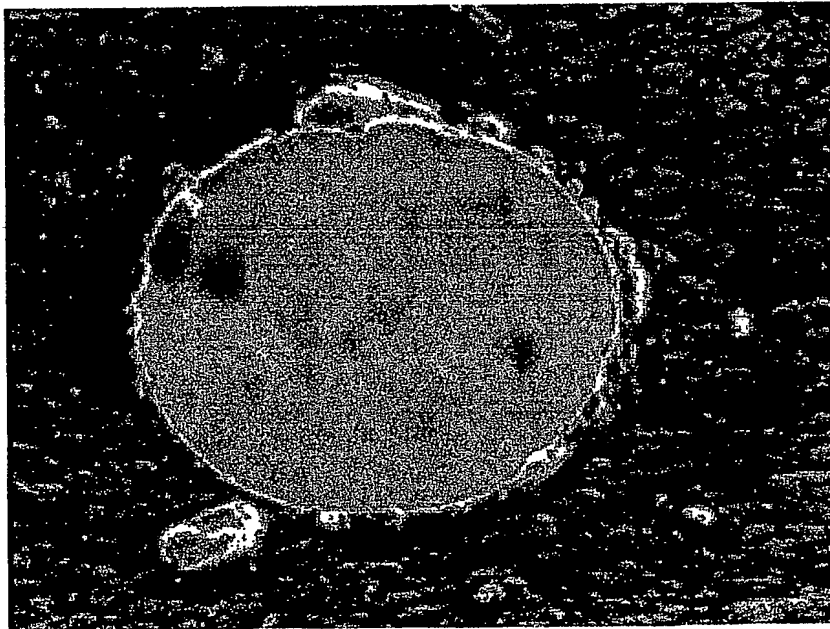


FIG. 7b



7/9

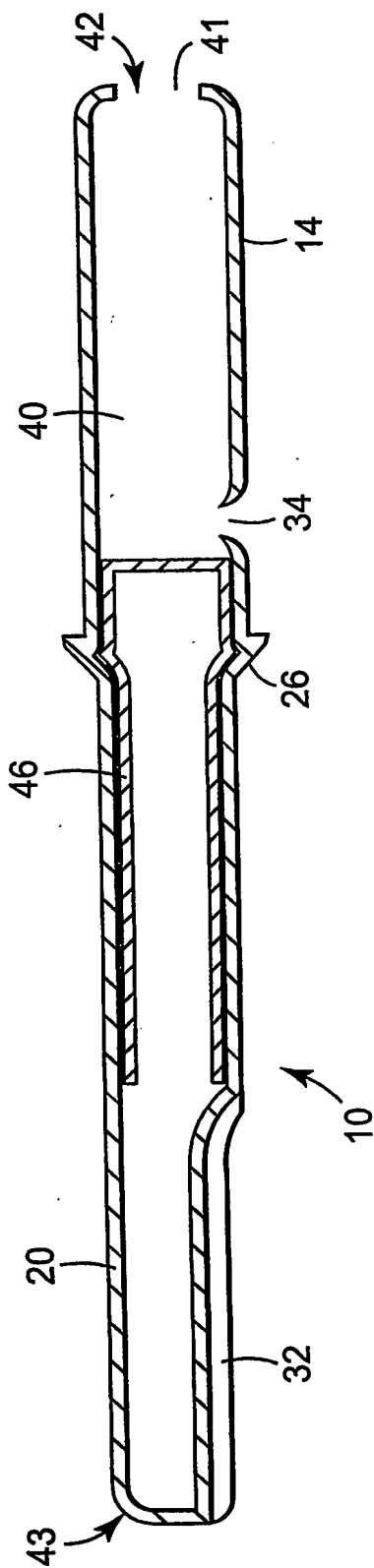


FIG. 8

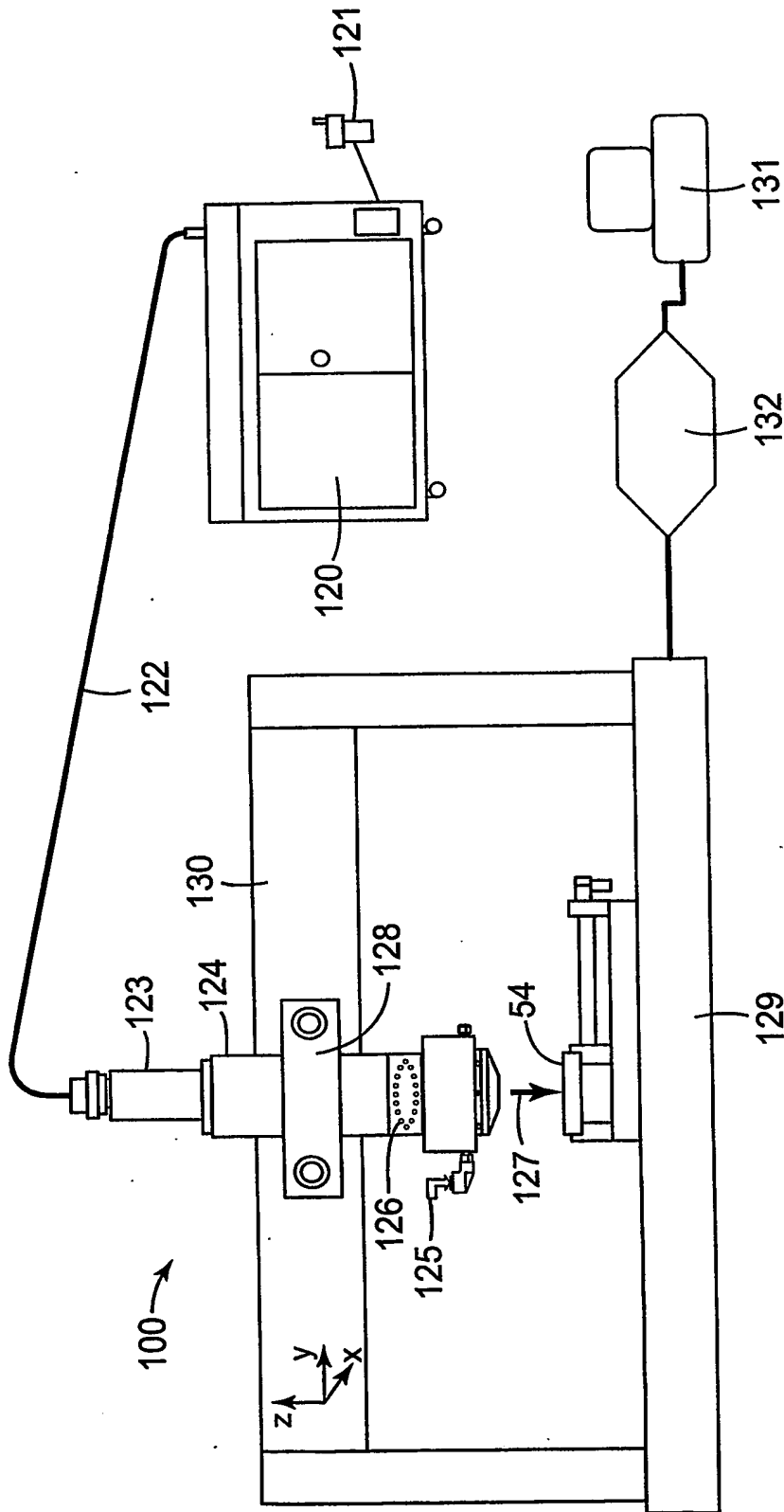


FIG. 9

9/9

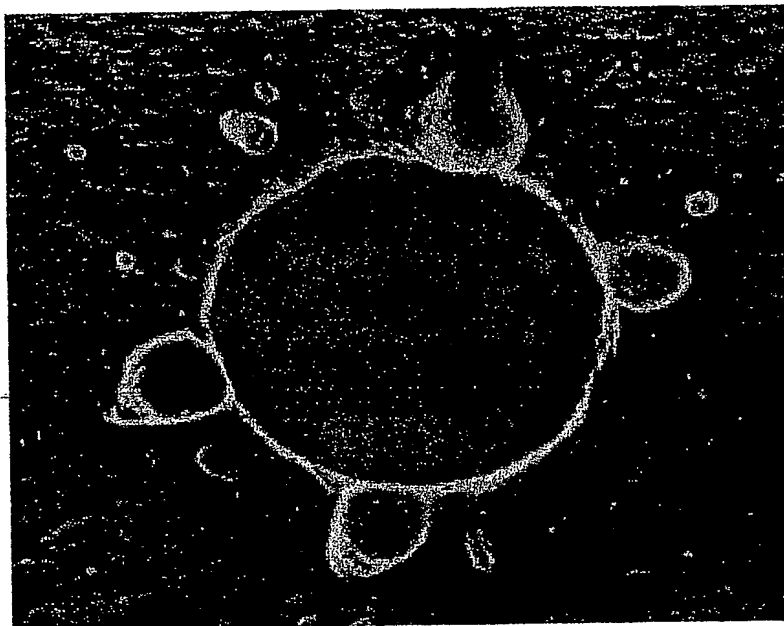


FIG. 10a

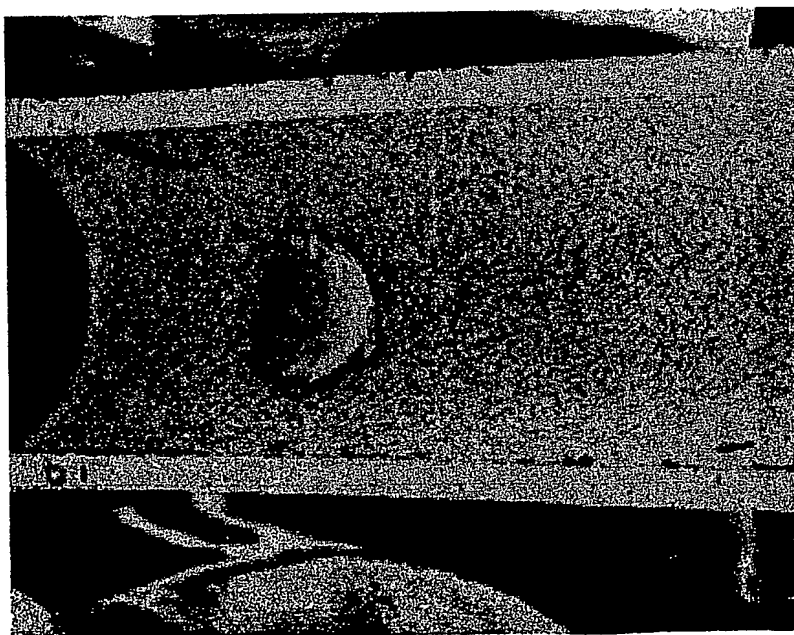


FIG. 10b

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 03/14468

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B23K26/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 99 55600 A (3M INNOVATIVE PROPERTIES CO) 4 November 1999 (1999-11-04) cited in the application page 3, line 13-18 page 9, line 30 -page 10, line 26; figure 2 page 13, line 19 -page 14, line 20; figure 3 ---	1-9, 11-14
Y	DE 39 37 460 A (DAIMLER BENZ AG) 8 November 1990 (1990-11-08) column 2, line 63 -column 3, line 42; figure 3 ---	1-9, 11-14
Y	WO 89 03274 A (AKAD TEKN VIDENSKABER) 20 April 1989 (1989-04-20) page 5, line 22 -page 6, line 10; figures 3,5 ---	1-9, 11-14
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* & * document member of the same patent family

Date of the actual completion of the international search

29 August 2003

Date of mailing of the international search report

04/09/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Christensen, J

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 03/14468

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>WO 00 69594 A (US ENRICHMENT CORP) 23 November 2000 (2000-11-23) page 5, line 11 -page 6, line 19; figure 1 -----</p>	<p>1-9, 11-14</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/14468

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9955600	A	04-11-1999	AT 245588 T	15-08-2003
			AU 738828 B2	27-09-2001
			AU 3670599 A	16-11-1999
			CA 2329900 A1	04-11-1999
			DE 69909771 D1	28-08-2003
			EP 1073594 A1	07-02-2001
			JP 2002512871 T	08-05-2002
			WO 9955600 A1	04-11-1999
DE 3937460	A	08-11-1990	DE 3937460 A1	08-11-1990
WO 8903274	A	20-04-1989	WO 8903274 A1	20-04-1989
WO 0069594	A	23-11-2000	WO 0069594 A1	23-11-2000
			AU 4004099 A	05-12-2000